Appendix D

Supplemental Exposure Assessment Information

D.1 Technical Memorandum RE: Modeling Worker Inhalation Exposure

D.2 Technical Memorandum RE: Sensitivity and Uncertainty Analysis of Workplace Air Concentration Models Used in the PWB Exposure Assessment

D.1   Technical Memorandum RE: Modeling Worker Inhalation Exposure

<p align="center">**TECHNICAL MEMORANDUM**</p>

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               PWB Project File, EPA # X823941-01-0

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DATE: December 22, 1995   (Revised 8/96)

RE: **MODELING WORKER INHALATION EXPOSURE**

I.   INTRODUCTION

This technical memorandum is submitted for review by the RM2 work group. Air transport models to estimate worker inhalation exposure to chemicals from printed wiring board (PWB) making holes conductive (MHC) lines are presented here for review and comment. The purpose is to reach agreement on our technical approach before proceeding with further analysis.

Three air transport models will be required to estimate worker exposure:

!   Volatilization of chemicals induced by air sparging.

!   Aerosol generation induced by air sparging.

!   Volatilization of chemicals from the open surface of MHC tanks.

The total transport of chemicals from the air-sparged baths will be determined by summing the releases calculated using each of the three models described above. Air-sparged baths include the electroless-copper baths and some cleaning tanks. Only the third model will be applied to determine the atmospheric releases of chemicals from unsparged baths. This document includes a review of the relevant literature, descriptions of the models, and examples demonstrating the proposed use of the models. The results of the model calculations will be compared to available occupational monitoring data.

II.   VOLATILIZATION OF CHEMICALS FROM AIR-SPARGED PWB MANUFACTURING TANKS

Mixing in plating tanks, e.g., the electroless copper plating tank, is commonly accomplished by sparging the tank with air. This is similar to aeration in wastewater treatment plants, and the volatilization of chemicals from these plants has been the focus of recent research. The volatilization models used in that research are based on well accepted gas transfer theory, discussed below.

Background

Volatilization of chemicals from water to air has been investigated by many researchers (Liss and Slater, 1974; Smith *et al.*, 1980; Roberts, 1983; Peng *et al.*, 1993). In PWB manufacturing, volatilization due to air sparging of process tanks is expected to be one of the main pathways for contaminant transfer to the air. In bubble aeration systems, the volatilization rate is dependent upon the volumetric gas flow rate, partial pressure of the gas, and the mass transfer rate coefficient (Matter-Müller, 1981). The volatilization characteristics for different diffuser types and turbulent conditions were evaluated by Matter-Müller (1981), Peng (1995), and Hsieh (1994).

Volatilization from aerated systems has been mainly quantified using the two-film theory (Cohen *et al.*,1978; Mackay and Leinonen, 1975). This work is discussed below and is used to model chemical transfer rates from air-sparged PWB process tanks. The main assumption of the theory is that the velocity at a fluid interface is zero. Molecular diffusion across the interfacial liquid film is the limiting factor for mass transfer to the air, and it is used to develop a simple equation relating the overall mass transfer coefficient to the diffusion coefficient of the chemical in water.

The two-film model of gas transfer was expanded to include mass transfer in diffused aeration systems (Matter-Müller *et al.*, 1981). Matter-Müller *et al.* assumed that the system was isothermal, hydraulic conditions were steady, and that pressure and volume changes within the bubbles were negligible. Further, an overall mass transfer coefficient was applied to represent transfer of contaminants to the bubble as they rose through the homogeneous liquid volume. Parker (1993) demonstrated that liquid-phase concentration can be assumed constant during the rise time of the bubble. Under these assumptions, Matter-Müller *et al.* derived the following relationship predicting the mass transfer rate from an aerated system:

$$F_{y,s} = Q_G H_y c_{L,y} \left[1 - \exp\left(-\frac{K_{OL,y} a V_L}{H_y Q_G} \right) \right] \qquad (1)$$

where:

$F_{y,s}$ = mass transfer rate of chemical *y* out of the system by sparging (m/t)
Q_G = gas flow rate (l^3/t)
H_y = dimensionless Henry's constant for chemical *y*
$c_{L,y}$ = concentration of chemical *y* in bulk liquid (m/l^3)
$K_{OL,y}$ = overall mass transfer coefficient for chemical *y* (l/t)
a   = interfacial area of bubble per unit volume of liquid (l^2/l^3)

$$V_L \quad = \text{volume of liquid (l}^3\text{)}$$

The overall mass-transfer coefficient is defined as the inverse sum of the reciprocals of the liquid and gas-phase mass transfer coefficients; but, because molecular diffusion of oxygen and nonpolar organic substances is 10^3 times greater in air than in water (Matter-Müller *et al.*, 1981), it is set equal to the liquid phase coefficient only. The mass transfer coefficient of a chemical can then be related to oxygen using the following equation:

$$K_{OL,y} = \left(\frac{D_y}{D_{O2}} \right) K_{OL,O2} \tag{2}$$

where:

D_y = molecular diffusion coefficient for chemical y in water (l^2/t)
D_{O2} = molecular diffusion coefficient for oxygen in water (l^2/t)
= 2.1×10^{-5} cm^2/cm @ 25° C (Cussler, 1984)
$K_{OL,y}$ = overall mass transfer coefficient for chemical y (l/t)
$K_{OL,O2}$ = overall mass transfer coefficient for oxygen in water (l/t)

The value of $K_{OL,O2}$ at 25°C in diffused aeration systems can be estimated using a correlation developed by Bailey and Ollis (1977):

$$K_{OL,O_2} = 0.31 * \left(\frac{d_b^3 (\rho_{H2O} - \rho_{air}) g}{\mu_{H2O} D_{O2}} \right)^{1/3} \frac{D_{O2}}{d_b} \tag{3}$$

where:

d_b = bubble diameter (l)
ρ_{H2O} = density of water (m/l^3)
ρ_{air} = density of air (m/l^3)
g = gravitational constant (l/t^2)
μ_{H2O} = viscosity of water (m/l·t)

If a measured value of D_y is not available, then it can be calculated from the Hayduk and Laudie correlation (Lyman *et al.*, 1982):

$$D_y(cm^2/\text{sec}) = \frac{13.26 x 10^{-5}}{\mu_{H2O}^{1.14} V_m^{0.589}} \tag{4}$$

where:

V_m = molar volume of solute (cm^3/mol)
μ_{H2O} = viscosity of water (centipoise)

The mass transfer coefficient can be corrected for the bath temperature (°C) as follows (Tschabanoglous, 1991):

$$K_{OL,y,T} = K_{OL,y,25^oC} \ 1.024^{(T-25)} \tag{5}$$

Bailey and Ollis (1977) developed a relationship for the interfacial area per unit volume (a) as a function of the bubble diameter, gas flow rate, and tank geometry:

$$a = \frac{6 \ Q_G \ t_b}{V_L \ d_b} \tag{6}$$

where:

h = tank depth (l); and

$$t_b = \frac{18 \ h \ \mu_{H2O}}{d_b^2 \ (\rho_{H2O} - \rho_{air})g} \tag{7}$$

Values of H_y are often reported at 25°C. The Henry's constant can be corrected to the bath temperature using the van't Hoff equation:

$$H_{y,T} = H_{y,25^oC} \exp\left[\frac{\Delta H_{gas} - \Delta H_{aq}}{R} \left(\frac{1}{298.15} - \frac{1}{273.15 + T} \right) \right] \tag{8}$$

where:

$\Delta \eta_{gas}$ = enthalpy of the chemical in the gas phase (cal/mol)
ΔH_{aq} = enthalpy of the chemical in the aqueous phase (cal/mol)
R = gas constant (1.987 cal/mol·K)

Matter-Müller (1981) concluded that surfactants do not significantly alter the rate of volatilization from the water. Some agents did lower the overall mass transfer coefficient, but most showed no appreciable difference. This was attributed to an increase in the specific interfacial area, *a*, when the interfacial energy, or mass transfer coefficient, was decreased. The transfer rate of volatile organic compounds (VOCs) was found to depend heavily upon the type of aerators used, and the degree of saturation of the bubbles rising through the liquid.

III.   AEROSOL GENERATION FROM BATHS MIXED BY SPARGING WITH AIR

Aerosols or mists have been identified as a major source of contaminants released by electroplating baths to the atmosphere (Burgess, 1981) and should be investigated as a potential source of contaminants from electroless baths. At least two sources of aerosols exist in electroplating baths: 1) aerosols generated due to liquid dripping from parts as they are removed from the bath (drag-out drips); and 2) aerosols generated due to bursting of the bubbles at the surface. Drag-out drips are insignificant compared to other sources of aerosols (Berglund and Lindh, 1987; Cooper et al., 1993).

Bubbles in electroplating baths can originate from the dissociation of water at the electrode, or mixing of the bath via air sparging. Bubbles in other plating baths (e.g., electroless plating baths) can originate from reactions in the bath or mixing of the bath via air sparging. The rate of aerosol generation per unit bubble volume decreases with increasing bubble size. Bubbles generated by water dissociation are typically smaller than those generated by air sparging; therefore, aerosol generation in electroless plating processes may be less significant than in electroplating operations. The focus of this memo is aerosols generated by air sparging. Except for the conductive polymer and non-formaldehyde electroless alternatives, MHC processes in PWB manufacturing do not use electroplating and therefore would not dissociate water to form gas bubbles. Information collection is continuing to allow prediction of aerosol formation in MHC processes that do have an electroplating step. Importantly, Berglund and Lindh (1987) report that aerosol generation from electroplating tanks is greatly reduced by sparging; the relatively large air bubbles formed during air sparging coalesce the smaller bubbles formed by hydrolysis and electroless plating reactions.

To estimate the emission of contaminants resulting from aerosols, the rate of aerosol generation and the concentration of contaminant in the aerosol are required. Limited information concerning the rate of aerosol formation was found in the literature. The following sources were consulted:

! U.S. EPA (1991). *Chemical Engineering Branch Manual for the Preparation of Engineering Assessments*.

! Chemical Abstracts, 1986 to date.

! Current and past text books in air pollution, chemical engineering, and water and wastewater treatment.

! Perry's Handbook (1984) related to entrainment in distillation trays.

! The last five years of *Water Environment Research* and *ASCE Journal of the Environmental Engineering Division*.

! A title key-word search of holdings in the library of the University of Tennessee.

! The ASPEN model commonly used for modeling chemical manufacturing processes. (It was found that any aerosol formation routines within ASPEN would be relevant to entrainment in devices such as distillation trays and not relevant to sparging of tanks.)

! The manager of the US EPA Center for Environmental Assessment Modeling in Athens, Georgia, as well as an expert in the Air and Energy Lab - Emission Modeling Branch in North Carolina.

In this work, the aerosol formation rates will be predicted based upon limited measurements of aerosol generation in electroplating (Berglund and Lindh, 1987) and other air-sparged baths (Wangwongwatana et al., 1988; Wangwongwatana et al., 1990) found in the literature.

Berglund and Lindh (1987) developed several graphs relating aerosol generation to air sparging rate (Figure 1a), bath temperature (Figure 1b), air flow rate above the bath (Figure 1c), and distance between bath surface and the tank rim (Figure 1d). Using Figures 1a-1d, the following relationship may be developed:

$$R_A = \left[5.5x10^{-5}\left(Q_G / A\right) + 0.01\right] F_T \, F_A \, F_D$$

(9)

where:

R_A = aerosol generation rate (ml/min/m^2)
Q_G/A = air sparging rate per unit bath area (l/min/m^2)
F_T = temperature correction factor
F_A = air velocity correction factor
F_D = distance between the bath surface and tank rim correction factor

Wangwongwatana et al. (1988) presented figures relating the number of aerosol droplets generated as a function of air flow rate, bubble rise distance, bubble size, and colloid concentration (Figure 2). Droplet size distribution measurements by these researchers indicate volume mean diameters of 5 to 10 μm. The aerosol generation rate can be calculated using the following equation:

$$R_A = \frac{Q_G C_d V_d}{A}$$

(10)

where:

C_d = droplet concentration (l^{-3})
V_d = droplet volume (l)
A = bath area (l^2)

Contaminants may be present in aerosols at elevated concentration relative to the bath concentration. Colloidal contaminants may be collected on the bubble surface as it rises through the bath. As the bubble bursts, the contaminants on the bubble surface are incorporated into aerosols. Wangwongwatana et al. (1990) report that in their experiments about one in two aerosols contain polystyrene latex spheres, compared to about one in 250 expected based upon the concentration of latex sphere in the bath. Organic contaminants may also partition at the air-water interface. A correlation for the water-interface partitioning coefficient for nonpolar compounds, k_{IW}, defined as the ratio of the mass of contaminant per unit area of interface to the mass of contaminant per unit volume of water is given by Hoff et al. (1993):

$$\log k_{IW} = -8.58 \, -0.769 \, \log C_W^S$$

(11)

where:

C_W^S = saturated aqueous solubility of the contaminant.

For more polar compounds a more complicated relationship is required:

$$\log k_{IW} = -7.508 + \log \gamma_w + a_s(\sigma_{wa} - \sigma_{sa} - 1.35\sigma_{sw})/2.303RT \tag{12}$$

where:

γ_w = activity coefficient of the contaminant in water (dimensionless)
a_s = molar area of the solute (cm^2/mol)
R = gas constant (8.314×10^7 erg/mol K)
F_{WA} = surface tension of the water-air interface (dyne/cm)
F_{SA} = surface tension of the solute-air interface (dyne/cm)
F_{SW} = surface tension of the solute-water interface (dyne/cm)

Hoff et al. (1993) also present a relationship for the ratio of the mass of contaminant sorbed at the air-water interface to the mass of contaminant in the gas volume of the bubble:

$$\frac{M_I}{M_b} = \frac{k_{IW}}{H_y(d_b / 6)} \tag{13}$$

where:

M_I = mass of contaminant at the interface
M_b = mass of contaminant in gas bubble

Only a small fraction of the bubble interface will be ejected as aerosols. It may be calculated from the following equation:

$$f_{IE} = \frac{R_A \ A \ d_b}{6 \ Q_G \ l_b} \tag{14}$$

where:

f_{IE} = fraction of bubble interface ejected as aerosols (dimensionless)
l_b = thickness of bubble film (l)

The rate of mass transfer from the tank to the atmosphere by aerosols, $F_{y,a}$ (m/t) is given by:

$$F_{y,a} = \frac{M_I}{M_b} f_{IE} \ F_{y,s} \tag{15}$$

IV. VOLATILIZATION OF CHEMICALS FROM THE OPEN SURFACE OF MHC TANKS

Most plating tanks have a free liquid surface from which chemicals can volatilize into the workplace air. Air currents across the tank will accelerate the rate of volatilization. The model presented in the Chemical Engineering Branch Manual for the Preparation of Engineering Assessments (CEBMPEA) (US EPA, 1991) has potential application in this case. Some limitations of the model should be pointed out. The model was developed to predict the rate of

volatilization of pure chemicals, not aqueous solutions. The model was also validated using pure chemicals. As a result, the model implicitly assumes that mass transfer resistance on the gas side is limiting. The model may fail in describing volatilization of chemicals from solutions when liquid-side mass transfer controls.

CEBMPEA models the evaporation of chemicals from open surfaces using the following model:

$$F_{y,o} = 2\ c_{L,y}\ H_y\ A\ [D_{y,air}v_z/(\pi z)]^{0.5} \tag{16}$$

where:

$F_{y,o}$ = volatilization rate of chemical y from open tanks (m/t)
$D_{y,air}$ = molecular diffusion coefficient of chemical y in air (l^2/t)
v_z = air velocity (l/t)
z = distance along the pool surface (l)

The value of v_z recommended by CEBMPEA is 100 ft·min^{-1}. The value of $D_{y,air}$ can be estimated by the following formula (US EPA, 1991):

$$D_{y,air} = 4.09\text{x}10^{-5}\ T^{1.9}\ (1/29 + 1/M)^{0.5}\ M^{-0.33}/P_t \tag{17}$$

where:

$D_{y,air}$ = molecular diffusion coefficient of chemical y in air (cm^2/s)
T = air temperature (K)
M = molecular weight (g/mol)
P_t = total pressure (atm)

This equation is based on kinetic theory and generally gives values of $D_{y,air}$ that agree closely with experimental data.

V. CALCULATION OF CHEMICAL CONCENTRATION IN WORKPLACE AIR FROM EMISSION RATES

The indoor air concentration will be estimated from the following equation (US EPA, 1991):

$$C_y = F_{y,T}/(V_R\ R_V\ k) \tag{18}$$

where:

C_y = workplace contaminant concentration (m/l^3)
$F_{y,T}$ = total emission rate of chemical from all sources (m/t)
V_R = room volume (l^3/t)
R_V = room ventilation rate (t^{-1})
k = dimensionless mixing factor

The mixing factor accounts for slow and incomplete mixing of ventilation air with room air. CEBMPEA sets this factor to 0.5 for the typical case and 0.1 for the worst case. CEBMPEA commonly uses values of the ventilation rate Q from 500 ft^3/min to 3,500 ft^3/min. Appropriate

ventilation rates for MHC lines will be chosen from facility data and typical industrial recommendations.

VI. EXAMPLE MODELING OF FORMALDEHYDE RELEASE TO ATMOSPHERE FROM AIR-SPARGED ELECTROLESS COPPER BATH

In the examples below, the values of some parameters are based upon a site visit to SM Corporation in Asheville, NC. Except where stated otherwise, final values of the various parameters used in the models will be chosen based on the results of the Workplace Practices Questionnaire, chemical suppliers information, site visits, and performance demonstrations. All parameter values are based on preliminary information and are subject to change.

Values of site-specific parameters assumed in the example

Tank volume = 242 L	Site visit to SM Co., Asheville, NC
Tank depth = 71 cm	Assumed
Tank width = 48 cm	Assumed
Tank length = 71 cm	Assumed
Air sparging rate = 53.80 L/min	Midpoint of values given in Perry's Handbook, 1985, pg 19.13
Tank temperature = 51.67°C	Site visit to SM Co., Asheville, NC
H2CO Concentration in tank = 7,000 mg/L	Product data sheets
Bubble diameter at tank surface = 2.00 mm	Assumed
Room length = 20 m	Assumed
Room width = 20 m	Assumed
Room height = 5 m	Assumed
Air turnovers/hour = 4 hr^{-1}	Assumed
Air velocity across tank surface = 0.508 m/s	Default recommended by US EPA, 1991
Dimensionless mixing factor = 0.5	Default recommended by US EPA, 1991

Volatilization induced by air sparging

Calculating overall mass transfer coefficient for oxygen in water:

$$K_{OL,O_2} = 0.31 * \left(\frac{d_b^3(\rho_{H2O} - \rho_{air})g}{\mu_{H2O}D_{O2}} \right)^{1/3} \frac{D_{O2}}{d_b}$$

$$= 0.0113 \text{ cm/sec}$$
$$= 0.678 \text{ cm/min}$$

where:

d_b = 0.2 cm
ρ_{H2O} = 0.997 g/cm^3 (Dean, 1985)
ρ_{gas} = 0.00118 g/cm^3 (Dean, 1985)
g = 980 cm/sec^2

μ_{H2O} = 0.0089 (g/cm·sec) (Dean, 1985)
D_{O2} = 2.1x10^{-5} cm^2/sec (Cussler, 1984)

Calculating molecular diffusion coefficient of formaldehyde in water:

$$D_y = \frac{13.26x10^{-5}}{\mu_{H2O}^{1.14} \; V_m^{0.589}}$$

$$= 1.81x10^{-5} \; cm^2/sec$$

where:
V_m = 36.8 cm^3/mol
μ_{H2O} = 0.89 centipoise

Calculating mass transfer coefficient of formaldehyde in water:

$$K_{OL,y} = \left(\frac{D_y}{D_{O2}}\right) K_{OL,O2} = \left(\frac{1.81x10^{-5}}{2.10x10^{-5}}\right) * 0.678$$

$$= 0.584 \; cm/min$$

Correcting mass transfer coefficient for temperature:

$K_{OL,y, 51.67} = K_{OL,y,25^{o}C} \; 1.024^{(T-25)} = 0.584*1.024^{(51.67-25)} = 1.10$ cm/min

Calculating t_b:

$$t_b = \frac{18 \quad h \; \mu_{H2O}}{d_b^2 \; (\rho_{H2O} - \rho_{air})g}$$

$$= 0.291 \; sec$$
$$= 4.85x10^{-3} \; min$$

where:
h = 71 cm

Calculating interfacial area per unit volume:

$$a = \frac{6 \; Q_G \; t_b}{V_L \; d_b}$$

$$= 0.0323 \; cm^2/cm^3$$

where:

$$Q_G \quad = 53,800 \text{ cm}^3/\text{min}$$
$$V_L \quad = 242,000 \text{ cm}^3$$

Correcting Henry's constant for temperature:

$$H_{y,51.67} = H_{y,25^oC} \exp\left[\frac{\Delta H_{gas} - \Delta H_{aq}}{R} \left(\frac{1}{298.15} - \frac{1}{273.15 + T} \right) \right]$$

$$= 1.99 \times 10^{-5} \text{ (dimensionless)}$$

where:

$H_{y,25}{}^oC = 1.7 \times 10^{-7}$ atm·m^3/mol (Risk Assistant, 1995)

$\qquad\qquad = 6.38 \times 10^{-6}$ (dimensionless)

$DH_{gas} \quad = -27,700$ cal/mol

$DH_{aq} \quad = -35,900$ cal/mol

$R \qquad = 1.987$ cal/mol·K

Calculating mass transfer rate of formaldehyde by air sparging:

$$F_{y,v} \;=\; Q_G \; H_y \; c_{L,y} \left[1 - \exp\left(-\frac{K_{OL,y} a V_L}{H_y Q_G} \right) \right]$$

$$= 7.49 \text{ mg/min}$$

The argument of the exponential function is -8031. This indicates that the formaldehyde concentration in the air bubbles is essentially in equilibrium with the bath concentration.

Transport in aerosols

The aerosol generation rate will be estimated using data presented by both Berglund and Lindh (1987) and Wangwongwatana et al. (1988).

Calculating aerosol generation rate using Berglund and Lindh (1987) data:

$$R_A \;=\; \left[5.5 \times 10^{-5} \left(Q_G/A \right) + 0.01 \right] F_T \; F_A \; F_D$$

$$= 0.0187 \text{ mL/min/m}^2$$

where:

$Q_G/A \quad = (53.8 * 10,000)/(71 * 48) = 158$ (L/min/m^2)

$F_T \qquad = 0.95$ @ 51.67°C (Figure 1b)

$F_A \qquad = 1.2$ @ 0.508 m/s (Figure 1c)

$F_D \qquad = 1.0$ assumed (Figure 1d)

Calculating aerosol generation rate using Wangwongwatana et al. (1988) data:

The air sparging rate used in the example (53.8 L/min) must be converted to an equivalent rate in the experimental apparatus using the ratio of the area of the example bath (0.341 m^2) to the area of the experimental apparatus (0.123 m^2). The equivalent rate is 19.4 L/min. The bubble rise distance would be approximately 0.6 m. From Figure 2, it can be inferred that the droplet concentration is not much greater than 100 droplets/cm^3. The aerosol generation rate can now be calculated:

$$R_A = \frac{Q_G C_d V_d}{A}$$

$$= 8.27 \times 10^{-3} \text{ ml/m}^2/\text{min}$$

where:

Q_G = 53800 cm^3/min
C_d = 100 droplets/cm^3
V_d = (p/6) d$_d^3$ = 5.24$\times 10^{-10}$ cm^3
d_d = 0.001 cm (upper end of range reported by Wangwongwatana et al., 1988)
A = 0.341 m^2

The aerosol generation rates calculated by the two methods agree quite well. The model of Berglund and Lindh (1987) will be used because it gives a slightly greater generation rate and is easier to use.

Emission rate from bath. If it is assumed that the formaldehyde concentration in the aerosols is equal to the bath concentration (7 mg/mL) then the formaldehyde emission rate is:

$$F_{y,a} = (7 \text{ mg/mL}) \cdot (0.0187 \text{ mL/m}^2/\text{min}) \cdot (0.341 \text{ m}^2) = 4.46 \times 10^{-2} \text{ mg/min}$$

To determine if accumulation of the contaminant at the air-water interface is significant, k_{IW} must be estimated using Equation 11. Since formaldehyde is a gas at the temperatures of interest, interfacial tension data are not available; however, average values of other aldehydes may be used (Hoff et al., 1993). Calculation of k_{IW} @25°C is summarized below; information was not available for calculating k_{IW} at other temperatures.

$$\log k_{IW} = -7.508 + \log \gamma_w + a_s(\sigma_{wa} - \sigma_{sa} - 1.35\sigma_{sw}) / 2.303RT$$

$$= -6.848$$

where:

γ_w = 1.452 Method 1, page 11-10 in Lyman et al. (1982)
a_s = 9.35$\times 10^8$ cm^2/mol Calculated from: a_s = 8.45$\times 10^7$ V$_m^{2/3}$
R = 8.314$\times 10^7$ erg/mol K
σ_{WA} = 72 dyne/cm Hoff et al. (1993)
σ_{SA} = 21.9 dyne/cm Value for acetaldehyde, Weast, 1980
σ_{SW} = 14.6 dyne/cm Average value for n-heptaldehyde and benzaldehyde, Girfalco and Good, 1957
k_{IW} = 1.418$\times 10^{-7}$ cm

Formaldehyde emissions due to aerosols can now be calculated:

Calculating the ratio of contaminant mass sorbed at the air-water interface to mass in gas volume of bubble:

$$\frac{M_I}{M_b} = \frac{k_{IW}}{H_y(d_b/6)}$$

$$= 0.2138$$

Calculating fraction of bubble interface ejected as aerosols:

$$f_{IE} = \frac{R_A}{6} \frac{A}{Q_G} \frac{d_b}{l_b}$$

$$= 4.35 \times 10^{-3}$$

where:

l_b $= 5 \times 10^{-7}$ cm (Rosen, 1978)

Calculating formaldehyde mass transfer rate via aerosols from tank to the atmosphere:

$$F_{y,a} = \frac{M_I}{M_b} f_{IE} F_{y,s}$$

$$= 0.00697 \text{ mg/min}$$

Volatilization from open tanks

Calculating molecular diffusion coefficient of formaldehyde in air:

$$D_{y,air} = 4.09 \times 10^{-5} \, T^{1.9} \, (1/29 + 1/M)^{0.5} \, M^{-0.33} / P_t$$

$$= 0.174 \text{ cm}^2/\text{sec}$$

where:

    T $= 298.15$ K
    M $= 30.03$ g/mol
    P_t $= 1$ atm

Calculating volatilization rate of formaldehyde from open tanks:

$$F_{y,o} = 2 \, c_{L,y} \, H_y \, A \, [D_{y,air} v_z/(pz)]^{0.5}$$

$$= 13.8 \text{ mg/min}$$

where:

$D_{y,air}$ = molecular diffusion coefficient of chemical in air (l^2/t)
V_z = 0.508 m/sec
z   = 0.48 m (shortest tank dimension gives highest mass transfer rate)

The gas side mass transfer coefficient (k_g) in the above model is:

$$k_g = 2[D_{y,air}v_z/(pz)]^{0.5}$$

$$= 0.484 \text{ cm/sec}$$

Thibodeaux (1979) reports a value of the liquid side mass transfer coefficient (k_i) in large water bodies of about 6×10^{-4} cm/sec for wind speeds of 0.5 m/sec. Although not directly applicable to the current situation, it can be used as a first estimate to determine the potential for liquid film resistance to control the mass transfer rate.

$$\text{Liquid side resistance} = H_y / k_l = 3.3\times10^{-2} \text{ sec/cm}$$

$$\text{Gas side resistance} = 1/k_g = 2.1 \text{ sec/cm}$$

It can be concluded that formaldehyde volatilization from open tanks is controlled by gas-side mass transfer resistance; therefore, the CEBMPEA equation appears to be valid. It should be noted that it may be necessary to consider liquid-side mass transfer resistance for chemicals with larger Henry's constants. In this case the CEBMPEA model would not be valid.

Surprisingly, volatilization due to air sparging is less significant than that from open tanks. Although the concentration of formaldehyde in the bubbles is high (virtually at equilibrium with the formaldehyde concentration in the bath), the volume of air sparged is small compared to the volume of room air flowing over the top of the tanks.

Concentration of formaldehyde in workplace air

C_y $= F_{y,T}/(V_R R_V k)$
   $= 0.326 \text{ mg/m}^3$
   $= 0.265 \text{ ppmv}$

where: $F_{y,T}$ = 7.49 mg/min + 0.421 mg/min + 13.8 mg/min = 21.71 mg/min
   V_R = 20 m · 20 m · 5 m = 2000 m^3
   R_V = 4 hr-1 = 0.0667 min^{-1}
   k   = 0.5

VII. COMPARISON OF PREDICTED FORMALDEHYDE CONCENTRATIONS IN WORKPLACE AIR TO MONITORING DATA

In this section, the concentrations of formaldehyde in the workplace air predicted by the model are compared to available monitoring data. The purpose of the comparison is not to validate the model but to determine if the modeling approach gives reasonable values of formaldehyde concentration. Model validation would require calculation of formaldehyde concentrations using the conditions specific to the monitoring sites. Such data are not available.

The results of an OSHA database (OCIS) search of monitoring data for formaldehyde (provided by OPPT) include 43 measured air concentrations for 10 facilities in Standard Industrial Classification (SIC) 3672 (printed circuit boards). The concentrations range from not detected to 4.65 ppmv. Most of the concentrations (37/42) range from $\leq$ 0.04 to 0.6 ppmv, with all but one less than 1.55 ppmv. Cooper et al. reports formaldehyde concentrations from three electroless plating operations measured over a two day period. The mean concentrations ranged from 0.088 to 0.199 ppmv. The predicted concentration of formaldehyde in the workplace air was 0.263 ppmv. Thus the predicted value is within the range of concentrations determined by monitoring, and less than the OSHA time-weighted-average concentration of 0.75 ppmv. The authors conclude that the results are reasonable.

REFERENCES

Bailey and Ollis. *Biochemical Engineering Fundamentals.* New York: McGraw-Hill, Inc., 1977.

Berglund, R. and E. Lindh. "Prediction of the Mist Emission Rate from Plating Baths." *Proc. Am. Electroplaters and Surface Finishers Soc. Annu. Tech. Conf.,* 1987.

Burgess, W.H. *Recognition of Health Hazards in Industry: A Review of Materials and Processes.* New York: John Wiley and Sons, 1981.

Cohen, Y. and W. Cocchio. Laboratory Study of Liquid-Phase Controlled Volatilization Rates in Presence of Wind Waves. *Environ. Sci. Technol.*, **12**:553, 1978.

Cooper, C.D., R.L. Wayson, J.D. Dietz, D. Bauman, K. Cheze and P.J. Sutch. *Atmospheric Releases of Formaldehyde from Electroless Copper Plating Operations.* Proceedings of the 80th AESF Annual Technical Conference, Anaheim, CA. 1993.

Cussler, E.L. *Diffusion: Mass Transfer in Fluid Systems.* Cambridge: Cambridge University Press, 1984.

Dean, J.A. (Ed). *Lange's Handbook of Chemistry*, 13th ed. New York: McGraw Hill, 1985.

Girifalco, L.A. and R.J. Good. "A Theory for the Estimation of Surface and Interfacial Energies: I. Derivation and Application to Interfacial Tension." *J. Phys. Chem.,* **61**(7):904-909, 1957.

Hoff, J.T., D. Mackay, R. Gillham and W.Y. Shiu. "Partitioning of Organic Chemicals at the Air-Water Interface in Environmental Systems." *Environ. Sci. Technol.,* **27**(10):2174-2180, 1993.

Hsieh, C., R. Babcock and M. Strenstrom. Estimating Semivolatile Organic Compound Emission Rates and Oxygen Transfer Coefficients in Diffused Aeration. *Water Environ. Research*, **66**:206, 1994.

Liss, P.S. and P.G. Slater. Flux of Gases Across the Air-Sea Interface. *Nature*, **247**:181, 1974.

Lyman, W.J., W.F. Reehl and D.H. Rosenblatt. *Handbook of Chemical Property Estimation Methods,* Washington DC: American Chemical Society, 1982.

Mackay, D. and P.J. Leinonen. Rate of Evaporation of Low Solubility Contaminants from Water Bodies to Atmosphere. *Environ. Sci. Technol.*, **9**:1178, 1975.

Matter-Müller, C., W. Gujer and W. Giger. *Transfer of Volatile Substances from the Water to the Atmosphere*. Institute for Water Resources and Water Pollution Control (EAWAG), Swiss Federal Institute of Technol., CH-8600 Dubendorf, Switzerland, **15**:1271, 1981.

Parker, W., D. Thompson and J. Bell. Fate of Volatile Organic Compounds in Municipal Activated Sludge Plants. *Water Environ. Research*, **65**:58, 1993.

Peng, J., J.K. Bewtra and N. Biswas. Transport of High-Volatility Chemicals from Water into Air. *Proceeding of 1993 Joint CSCE-ASCE National Conf. on Environmental Eng.*, **120**:662, 1993.

Peng, J., J. Bewtra and N. Biswas. Effect of Turbulence on Volatilization of Selected Organic Compounds from Water, *Water Environ. Research*, **67**:000, 1995.

Perry, R.H., D.W. Green and J.O. Maloney (Eds). *Perry's Chemical Engineers' Handbook*, New York: McGraw-Hill Book Company, 1984.

Risk Assistant Software. Alexandria, VA: Thistle Publishing, 1995.

Roberts, P.V., P. Dandliker and C. Matter-Müller. *Volatilization of Organic Pollutants in Wastewater Treatment-Model Studies*, EPA-R-806631. U.S. EPA, Munic. Environ. Res. Lab., Cincinnati, Ohio, 1983.

Rosen, M.J. *Surfactants and Interfacial Phenomena.* New York: John Wiley & Sons, 1978.

Smith, J. H., D.C. Bomberger and D.L. Haynes. Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies, *Environ. Sci. Technol.*, **14**:1332, 1980.

Thibodeaux, L.J. *Chemodynamics: Environmental Movement of Chemicals in Air, Water and Soil.* New York: John Wiley & Sons, 1979.

Tschabanoglous, G. and F.L. Burton. *Wastewater Engineering: Treatment, Disposal, and Reuse*. New York: McGraw-Hill, Inc., 1991.

U.S. Environmental Protection Agency. *Chemical Engineering Branch Manual for the Preparation of Engineering Assessments*. Washington, DC: U.S. EPA Office of Toxic Substances. February 28, 1991.

Wangwongwatana, S., P.V. Scarpino and K. Willeke. "Liquid-to-Air Transmission of Aerosols from a Bubbling Liquid Surface." *J. Aerosol Sci.,* **19**(7):947-951, 1988.

Wangwongwatana, S., P.V. Scarpino, K. Willeke and P.A . Baron. "System for Characterizing Aerosols from Bubbling Liquids." *Aerosol Sci. Technol.,* **13**(3):297-307, 1990.

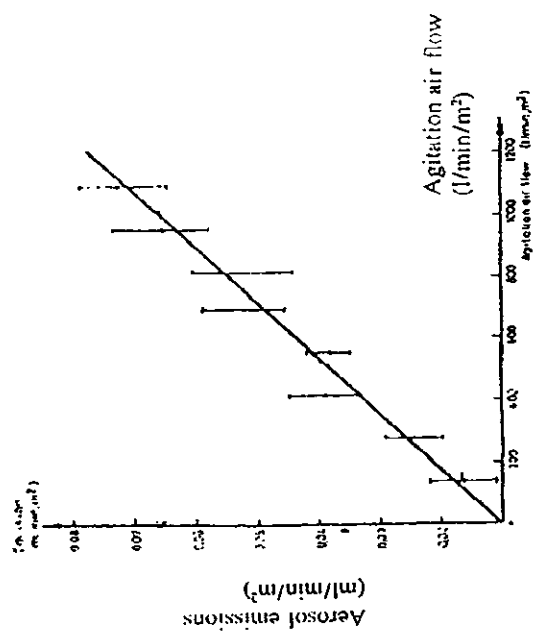Weast, R.C. (Ed.) *CRC Handbook of Chemistry and Physics*, 61st ed. Boca Raton, FL: CRC Press, 1980.
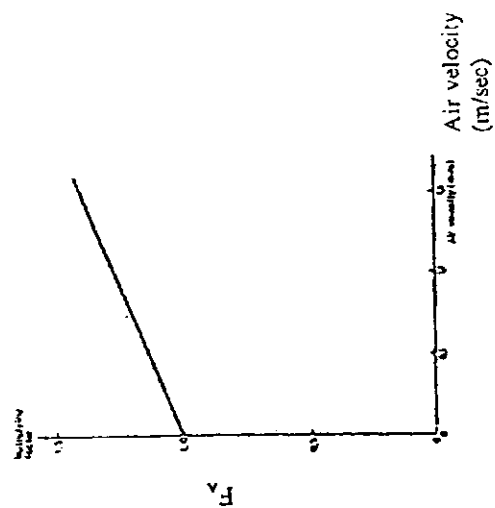
Figure 1a. Mist generation caused by air agitation.
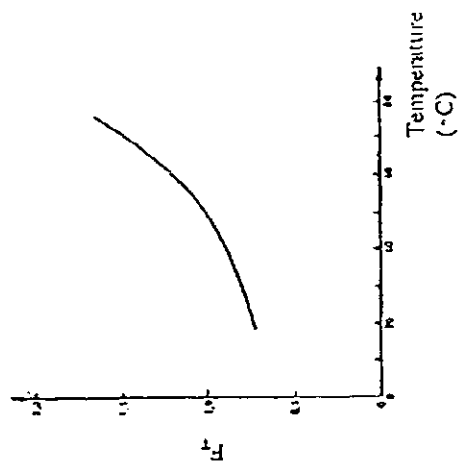

Figure 1b. Influence of bath temperature.

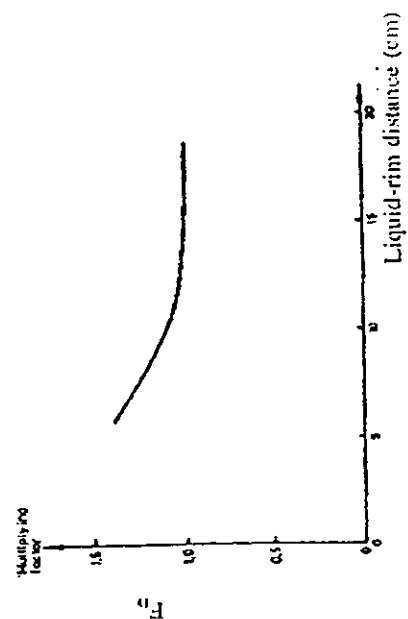Figure 1c. Influence of air velocity across the bath surface.

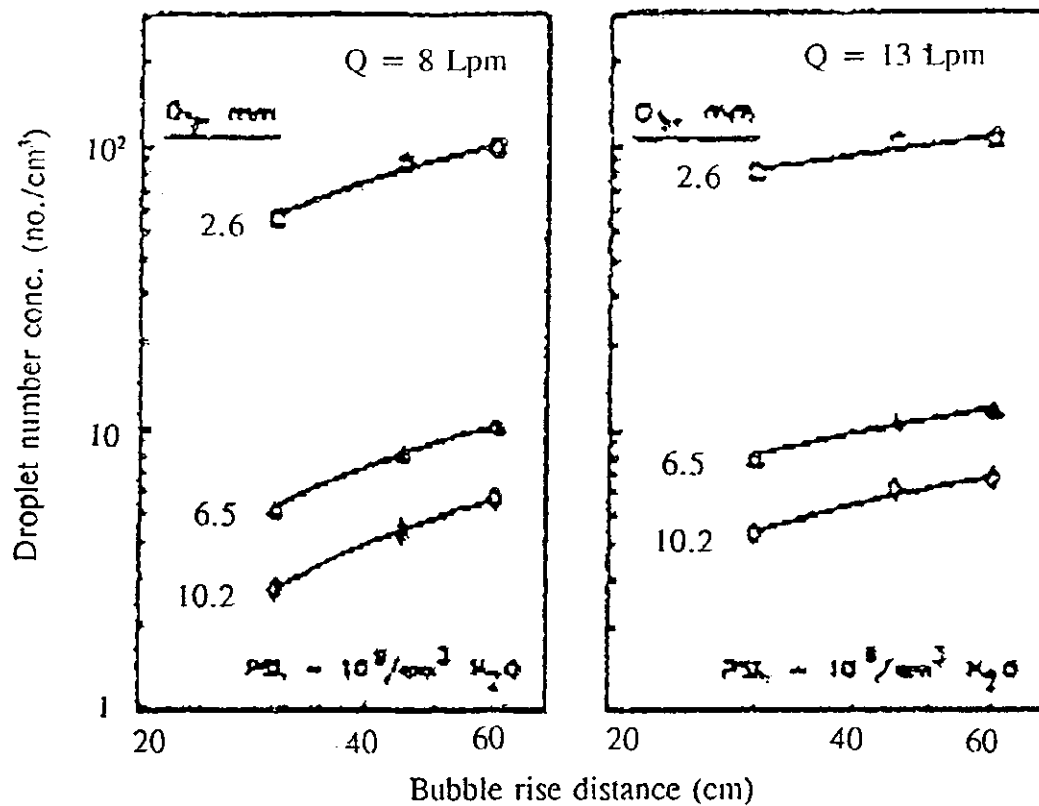Figure 1d. Influence of the distance from the liquid to the bath rim.

Figure 2. Effect of bubble rise distance on droplets number concentration. (From Wangwongwatana et al., 1990)

D.2   Technical Memorandum RE: Sensitivity and Uncertainty Analysis of Workplace Air Concentration Models Used in the PWB Exposure Assessment

TECHNICAL MEMORANDUM

TO: Kathy Hart / EPA DfE
               PWB Project File (Project # X823-941)

cc: Lori Kincaid

FROM   Nick Jackson, Mary Swanson, Bruce Robinson, Chris Cox

DATE: July 18, 1996 (revised August 8, 1996 and December 5, 1997)

RE: **SENSITIVITY AND UNCERTAINTY ANALYSIS OF WORKPLACE AIR CONCENTRATION MODELS USED IN THE PWB EXPOSURE ASSESSMENT**

I.   INTRODUCTION

This technical memorandum is submitted to the RM2 Work Group for review and comment. Sensitivity and uncertainty analyses of the fate and transport models used in predicting workplace air concentrations of MHC chemicals were performed. (These air concentrations are used in the exposure assessment to estimate worker inhalation exposures.) The model parameters having the greatest effect on chemical air concentrations in the workplace are identified. A quantitative uncertainty analysis was also performed. These analyses serve to pinpoint and validate key parameter assumptions.

II.   METHODS AND RESULTS

Sensitivity Analysis

The first step in this analysis was to determine the parameters in the air transport models that had the largest impact on the workplace chemical air concentrations regardless of parameter variability. This was done by independently varying each parameter in the model by a specific amount and observing the effect on chemical air concentration. This allows a comparison to be made between parameter importance in terms of model sensitivity because their effects on chemical air concentration were obtained independently of the other parameters.

Table 1 lists the parameters that had the greatest effect on workplace air concentration. Small changes in some parameters caused the model results to vary widely, indicating a need to determine the uncertainty associated with these variables. For sparged baths the example chemical was formaldehyde, and fluoboric acid was used for the unsparged bath analysis. Other

chemicals were observed in the sensitivity analysis to learn whether the effects per chemical would vary with these parameters. This means that every chemical will not be affected in exactly the same way when varying parameters, but will exhibit close behavior. This initial sensitivity analysis was used primarily to select the important parameters for the Monte Carlo Analysis to follow, and as a check for that analysis.

Table 1. Model Sensitivity to Parameters

Parameters (x)	Δx [1] (%)	Effects on Sparged Volatiles[2] (%)	Effects on Sparged Non-Volatiles[3] (%)	Effects on Un-Sparged Volatiles[4] (%)
Enthalpy (Aqueous or Gas)	10	-23.6	NA	-4.4
Bath Temperature	10	16.2	4.8	19.3
Henry's Law Constant (H_C)	10	10.0	NA	10.0
Bath Concentration of Chemical	10	10.0	10.0	10.0
Process Room Volume	10	-9.1	-9.1	-9.1
Air Turnover Rate	10	-9.1	-9.1	-9.1
Bath Surface Area	10	5.9	2.3	7.4
Air Sparging Rate	10	2.1	7.7	NA
Air Velocity Across Tank Surface	10	3.7	1.2	4.9
Molecular Weight	10	-2.0	NA	-2.1

1: Percentage increase in each parameter that produces corresponding percentage change in chemical room air concentration as shown in columns 2, 3, and 4.
2: Percentage increase or decrease in room air concentration of air-sparged volatiles due to parameter variation (Δx) of 10 percent.
3: Percent increase or decrease in room air concentration of air-sparged nonvolatile (i.e., vapor pressure $< 1 \times 10^{-3}$ torr) due to parameter variation (Δx) of 10 percent.
4: Percent increase or decrease in room air concentration of unsparged volatiles due to parameter variation (Δx) of 10 percent.

For example, a 10% increase in bath surface area increases a sparged volatiles' workplace air concentration by 5.9%, while only increasing a sparged non-volatile or salt air concentration by 2.3%. Each parameter listed was also increased by 20% to determine if its relationship to air concentration was highly nonlinear, but none exhibited a significant trend in this area. Parameters not listed in Table 1 exhibited negligible effects on the model (<0.001 percent change in air concentration). These negligible parameters are:

- Bath volume;
- Surface tension coefficients;
- Molecular volume;
- Water densities and viscosities (due to variation of temperature in baths);
- Sparged bubble diameter; and
- Correction factors in the Berglund and Lindh model (see Exposure Assessment Draft, 1996).

Monte Carlo Analysis

Overview and Approach. After evaluating the sensitivity of the model to each parameter the next step was to examine model sensitivity and uncertainty using Monte Carlo Analysis. This was done with a Monte Carlo software package (Crystal Ball, Decisioneering, Inc.) in conjunction with a spreadsheet program (Lotus 1-2-3). The air transport equations outlined in the Exposure Assessment Draft (May 15, 1996) were used with the distributions for each parameter from the Workplace Practices Survey to perform this Monte Carlo Analysis.

Many different methods are available to propagate parameter distributions through a model and analyze the results. However, the difficult task of correlating complex nonlinear models and their parameters with some kind of regression algorithm severely limits the available techniques. The Latin Hypercube modification of the Monte Carlo method is agreed upon by many researchers to be the best way to perform a sensitivity/uncertainty analysis of contaminant transport models. In Latin Hypercube sampling, a probability distribution is divided into intervals of equal probability, thereby allowing for a more precise sampling routine because the entire probability range is more consistently represented (Decisioneering, Inc.). This probabilistic approach was used to generate a distribution of possible workplace air concentrations in contrast to a single point estimate.

Table 2 lists the assumptions used for the parameter distributions for the two bath type examples and describes the sources of information.

Crystal Ball was used to produce two independent Monte Carlo simulations, one for volatiles in air-sparged baths and one for unsparged baths. The number of iterations used for each simulation was 15,000. This was chosen to ensure adequate convergence and stabilization of the tails on output distributions (based on McKone and Bogen, 1991). The mass flux contribution from nonvolatiles in sparged baths is largely negligible and is not included to simplify the Monte Carlo simulations.

In addition to probability distributions, Crystal Ball calculates the percent contribution each parameter makes to overall model variance by computing Spearman rank correlation coefficients between every assumption and model result while the simulation is running. Spearman rank correlation coefficients differ from traditional linear regressions because ranks are assigned to observations and then substituted for the actual numerical values in the correlation formula. This correlation has distinct advantages over a simple linear regression. The relationship between variables is no longer assumed to be linear, and no assumptions of normality are made concerning the distributions of the variables as the relationship is nonparametric (Walpole and Myers, 1993). This parameter analysis combines model sensitivity and variable uncertainty.

Table 2. Parameter Assumptions Used in Monte Carlo Forecast

Parameters	Sparged Bath	Unsparged Bath	Source of Data
Process Room Volume	Lognormal Dist. based on survey data[a]	Lognormal Dist. based on survey data[b]	Workplace Practices Survey Data
Process Area Air Turnover Rate	Lognormal Dist. based on survey data[a]	Lognormal Dist. based on survey data[b]	Workplace Practices Survey Data
k (EPA, 1991) dimensionless mixing factor	Point estimate 1.0	Point estimate 1.0	Comments, G. Froiman /EPA RM2 Workgroup; June 16, 1996
Henry's Law Constant (H_C)	Normal Dist. based on avail. data[a]	Normal Dist. based on avail. data[b]	ORNL and other chemical info sources
Chemical Conc. in Bath	Triangular Dist.[a]	Triangular Dist.[b]	MSDS and Supplier info
Bath Surface Area	Lognormal Dist. based on survey data[a]	Lognormal Dist. based on survey data[b]	Workplace Practices Survey Data
Bath Temperature	Normal Dist. based on survey data[a]	Normal Dist. based on survey data[b]	Workplace Practices Survey Data
Bath Volume	Normal Dist. based on survey data[a]	Normal Dist. based on survey data[b]	Workplace Practices Survey Data
Air Sparging Rate	Point estimate 53.8 L/min	Point estimate 53.8 L/min	Midpoint of avail. values - chosen after model sensitivity seen to be small
Bubble Diameter	Lognormal Dist. based on avail. information[a]	Lognormal Dist. based on avail. information[b]	allowed to vary largely with little effect
Air Velocity across Bath Surface	Point estimate 0.508 m/s	Point estimate 0.508 m/s	recommended by EPA
Distance across pool Surface	Square root of bath area from survey data	Square root of bath area from survey data	directly correlated with area Dist.
Enthalpies, Gas and Aqueous States	Point estimate -35.9 kcal/mol & -27.7 kcal/mol	Point estimate -35.9 kcal/mol & -27.7 kcal/mol	ORNL and other chemical info sources
Activity Coeff.	Point estimate 1.45	Point estimate 25	ORNL and other chemical info sources
Surface Tension Coefficients	Point estimate 72, 21.92, &14.6 dynes/cm^2	Point estimate 72, 28.85, & 35 dynes/cm^2	ORNL and other chemical info sources

a: Attachment A shows these parameter distribution functions.
b: Attachment B shows these parameter distribution functions.

Results. Two types of results are presented: probability distributions for modeled air concentrations and the Spearman Rank Correlation results. The probabilistic chemical air concentration curves for each type of bath are presented in Figures 1 and 2. An uncertainty chart for each bath identifies the parameters that contribute most to model variance (Figures 3 and 4).

The parameter that contributes most to model variance for both bath types is air turnover rate in the process area. The range and standard deviation of reported air turnover rates from the Workplace Survey is very high. This causes it to contribute more to model variance than the process room volume. The variability of the room volume data is low and keeps it from even appearing on this list, despite the model being equally sensitive to changes in volume or turnover

rate (as shown by Table 1). The chemical concentration in the bath is also high on the uncertainty charts because of the models' relative sensitivity to concentration and its variability.

Another important variable that appears on the sensitivity/uncertainty charts is bath temperature. This parameter is used to correct Henry's Law Constant (H_C) for temperature by an exponential relationship, but does not have much variability. H_C can also have a great effect on model outcome, depending upon the variability of the data. The distributions of H_C used here may not be entirely representative of the variation that can sometimes be encountered with this constant. For instance, Mackay (1991) has observed that a great deal of variation occurs with H_C when hydrophobic chemicals associate with the air-water interface and electrolytes or sorbents affect solubility in water. These variations are very difficult to characterize in a study unless H_C is measured under the conditions in question, which is not feasible here. Most chemical flux from sparged baths comes from the open surface volatilization equation (CEB, 1991), and will cause it to behave similarly to the unsparged bath equation as seen by results.

Comparison to Point Estimates. The probability distribution of formaldehyde air concentrations calculated by Monte Carlo Analysis were lower than expected from previously calculated point estimates. The 90th percentile from the frequency distribution is 0.61 mg/m^3, compared to 1.55 mg/m^3 calculated as a "high-end" point estimate (in the May, 1996, Exposure Assessment Draft). This suggests that the use of current point estimates results in a much more conservative air concentration than the 90th percentile. The point estimates in the exposure assessment use the 10th percentile air turnover rate, which controls air concentration because of its large variability shown in the uncertainty analysis.

A Monte Carlo distribution-based air turnover rate was determined using point estimates for all parameters and setting the air concentration equal to the 90th percentile probability frequency distribution from Crystal Ball. This was done for several chemicals in sparged and unsparged baths. This distribution-based air turnover rate was calculated as follows (from 3.3.1 in Exposure Assessment):

$$R_V = \frac{F_{Y,TOT}}{Conc \cdot V_R \cdot k}$$

where:

      Rv   = distribution-based air turnover rate (min^{-1})
      Fy,tot = total emissions from all air transport mechanisms (mg/min)
      Vr   = room volume (m^3)
      k   = dimensionless mixing factor (a default value of 1.0 was used)
      Conc = 90th percentile workplace air concentration from Monte Carlo Analysis (mg/m^3)
                 determined using complete distributions for all parameters

This calculated air turnover rate was 0.0211 min^{-1} for formaldehyde in a sparged bath compared to the 10th percentile air turnover rate of 0.0083 min^{-1}. To ascertain the dependence of this distribution-based air turnover rate on chemical and bath type (sparged or unsparged) this calculation was repeated several times. These calculated (distribution-based) air turnover rates were:

- 0.0210 min^{-1} for copper chloride in a sparged bath; and
- 0.0206 min^{-1} for fluoboric acid in an unsparged bath.

Because air concentration estimates become more conservative as air turnover rates decrease, the value of 0.021 min^{-1} is recommended for estimating air concentrations for all chemicals to best approximate 90th percentile air concentrations with the available data.

The results of this sensitivity analysis are consistent with those obtained by Fehrenbacher and Hummel (1996). They suggest default air turnover rates of 14 m^3/min for a bounding, or maximum, estimate of exposure with this equation. The default input value of ventilation rate for obtaining "what-if", or average estimates is 85 m^3/min (this value lies in the central portion of the range for the parameter). An air turnover rate of 0.021 min^{-1} corresponds to a ventilation rate of 23 m^3/min, when combined with room volume.

IV.   CONCLUSIONS

It is evident that a few parameters are key to modeling chemical flux from PWB tanks. These key parameters are:

- Air turnover rate;
- Bath temperature;
- Chemical concentration in bath; and
- Henry's Law Constant (H_C).

The air models' sensitivity to these parameters and their uncertainty provides a means of isolating them from less important variables. Isolating these variables allows for additional scrutiny to be placed upon the point estimate assumptions used for them in the volatilization models.

The air turnover rate assumption contributes most to overall model variance. The chemical bath concentration and bath temperature also contribute variance to the model, but are less important than air turnover rate. This statement is fortified by the fact that relatively accurate information is available on their distributions. H_C appears to be least important of the four, but may have more variability associated with it. The models appear to be largely indifferent to small changes in most other parameters.

A comparison of point estimates with the 90th percentile from Monte Carlo Analysis suggests that using the 10th percentile value for air turnover rate yields a point estimate that is highly conservative, and that an increased air turnover estimate of 0.021 min^{-1} would provide air concentration results closer to the 90th percentile.

V.   REFERENCES

Decisioneering, Inc. 1993. *Crystal Ball Software*.

Fehrenbacher, M.C. and A.A. Hummel. 1996. "Evaluation of the Mass Balance Model Used by the Environmental Protection Agency for Estimating Inhalation Exposure to New Chemical Substances." *American Industrial Hygiene Association*, **57**:526-536.

Mackay, D. 1991. *Multimedia Environmental Models: The Fugacity Approach*, Lewis Publishers, Inc.

McKone, T.E. and K.T. Bogen. 1991. "Predicting the Uncertainties in Risk Assessment: A California Groundwater Case Stud.," *Environmental Science & Technology*, **25**(10): 1674-1681.

U.S. Environmental Protection Agency. 1991. *Chemical Engineering Branch Manual for the Preparation of Engineering Assessments*. Washington, DC: U.S. EPA Office of Toxic Substances, February 28.

Walpole, R.E. and R.H. Myers. 1993. *Probability and Statistics for Engineers and Scientists*, New York: MacMillan Publishing Company.

Figure 1.
Forecast Probability Distribution from Monte Carlo Analysis for Sparged Bath Chemical Workplace Air Concentration in mg/m$^\wedge$3 (Formaldehyde)
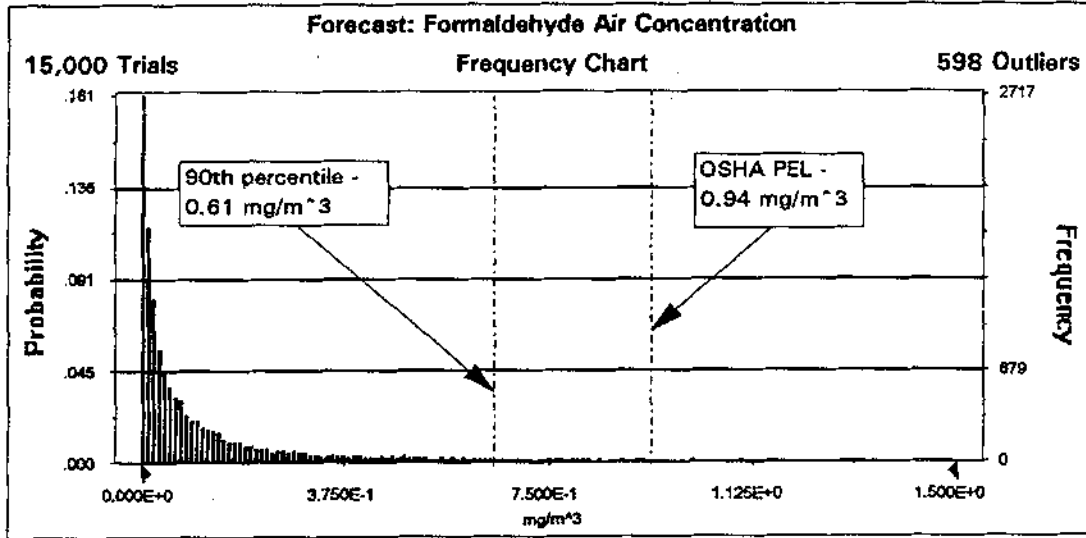
Percentiles:

Percentile	mg/m$^\wedge$3
0%	9.569E-05
10%	4.977E-03
20%	1.131E-02
30%	2.026E-02
40%	3.363E-02
50%	5.478E-02
60%	8.814E-02
70%	1.446E-01
80%	2.633E-01
90%	6.107E-01
100%	5.969E+01

Figure 2.
Forecast Probability Distribution from Monte Carlo Analysis for Unsparged Bath
Chemical Workplace Air Concentration in mg/m^ 3 (Fluoroboric Acid)

Forecast: Fluoboric Acid Air Concentration

| 15,000 Trials | Frequency Chart | 570 Outliers |
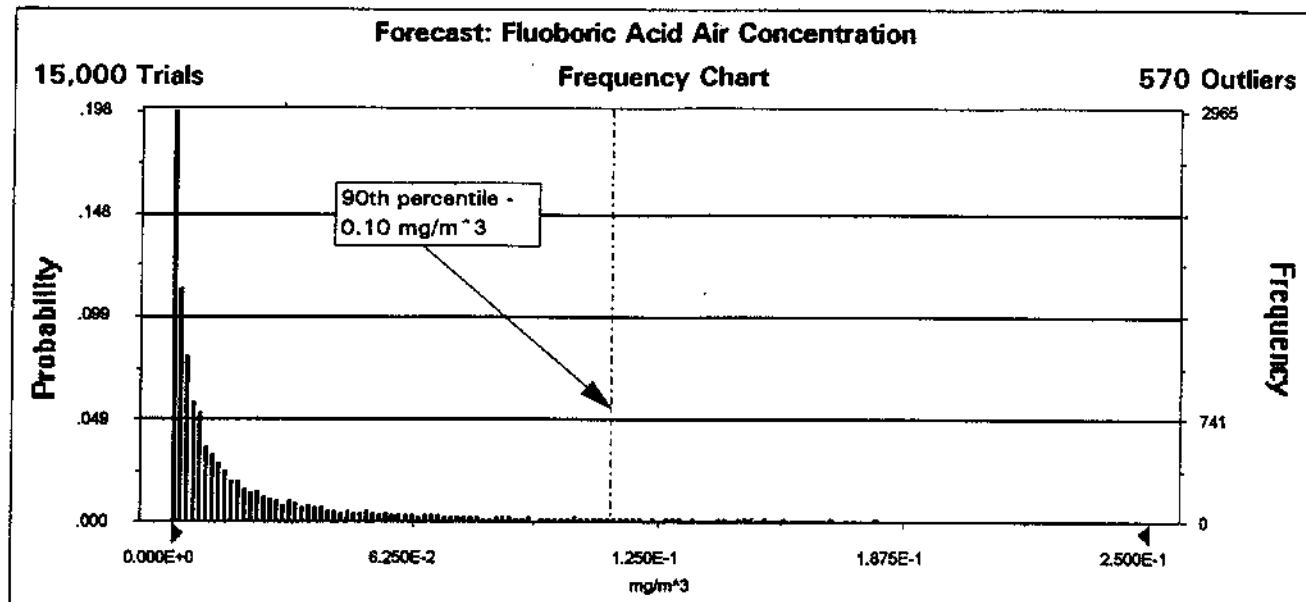
Percentiles:

Percentile	mg/m^3
0%	1.600E-05
10%	7.568E-04
20%	1.689E-03
30%	3.146E-03
40%	5.288E-03
50%	8.389E-03
60%	1.368E-02
70%	2.294E-02
80%	4.206E-02
90%	1.004E-01
100%	1.265E+01

Figure 3.
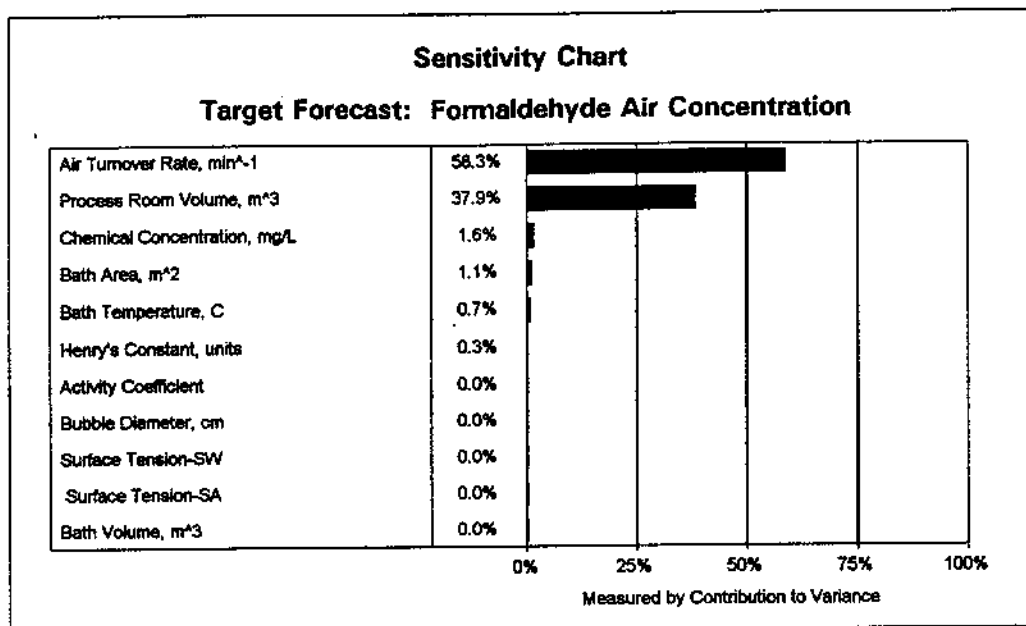## Sensitivity Chart for Sparged Bath Chemical Parameters Spearman Rank Correlation

Sensitivity Chart

Target Forecast: Formaldehyde Air Concentration

Air Turnover Rate, min^-1	56.3%
Process Room Volume, m^3	37.9%
Chemical Concentration, mg/L	1.6%
Bath Area, m^2	1.1%
Bath Temperature, C	0.7%
Henry's Constant, units	0.3%
Activity Coefficient	0.0%
Bubble Diameter, cm	0.0%
Surface Tension-SW	0.0%
Surface Tension-SA	0.0%
Bath Volume, m^3	0.0%

0%   25%   50%   75%   100%

Measured by Contribution to Variance

Figure 4.
Sensitivity Chart for Unsparged Bath Chemical Parameters Spearman Rank Correlation

Sensitivity Chart

Target Forecast: Fluoboric Acid Air Concentration

Air Turnover Rate, min^-1	57.2%	
Process Room Volume, m^3	36.7%	
Bath Area, m^2	2.9%	
Bath Temperature, C	1.6%	
Chemical Concentration, mg/L	1.3%	
Henry's Constant, units	0.4%	
Surface Tension-SA	0.0%	
Surface Tension-SW	0.0%	
Bath Volume, m^3	0.0%	
Bubble Diameter, cm	0.0%	
Activity Coefficient	0.0%	

0%   25%   50%   75%   100%

Measured by Contribution to Variance
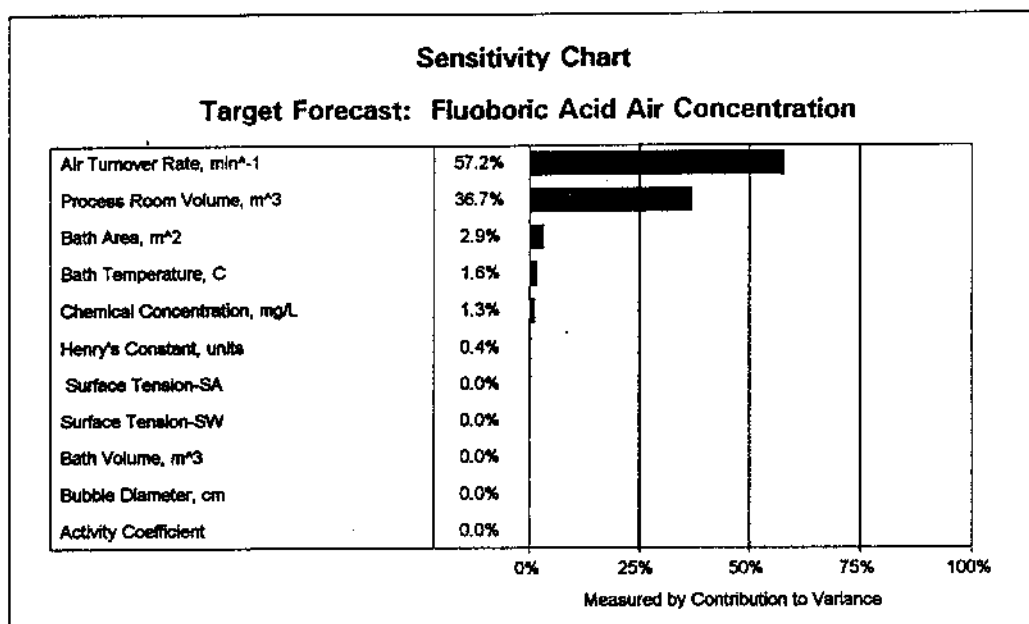
Figure 5.
Parameter Assumptions for Sparged Bath Monte Carlo Analysis - PDFs

Parameter: Process Room Volume, m^3
Lognormal distribution with parameters:

Geometric Mean	1,063.16
Geometric Std. Dev.	3.30

Selected range is from 33.00 to 17,000.00
Mean value in simulation was 1,911.23

Process Room Volume, m^3
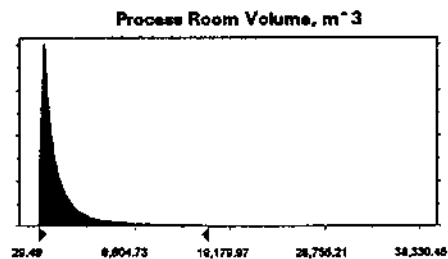
Parameter: Air Turnover Rate, min^-1
Lognormal distribution with parameters:

Mean	0.74
Standard Dev.	2.00

Selected range is from 0.00 to 10.10
Mean value in simulation was 0.64
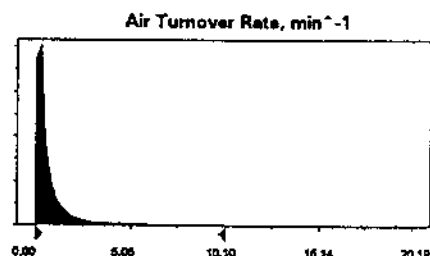
Air Turnover Rate, min^-1

Parameter: Chemical Concentration in Bath, mg/L
Triangular distribution with parameters:

Minimum	1580
Likeliest	3680
Maximum	5600

Selected range is from 1580 to 5600
Mean value in simulation was 3620

Chemical Concentration, mg/L
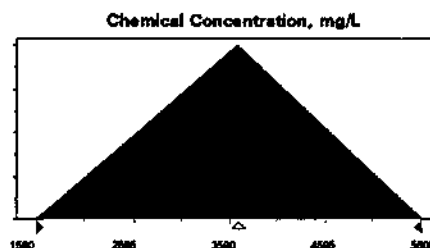
Parameter: Henry's Constant, atm*m^3/mol
Normal distribution with parameters:

Mean	2.35E-07
Standard Dev.	2.35E-08

Selected range is from -Infinity to + Infinity
Mean value in simulation was 2.35E-7

Henry's Constant, units
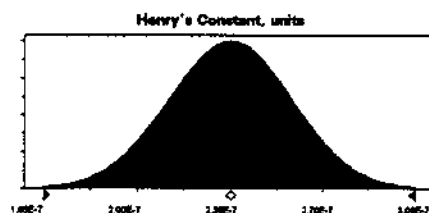
Parameter: Bath Temperature, degrees C
Normal distribution with parameters:

Mean	38.89
Standard Dev.	3.89

Selected range is from 20.00 to 58.00
Mean value in simulation was 38.89

Bath Temperature, C
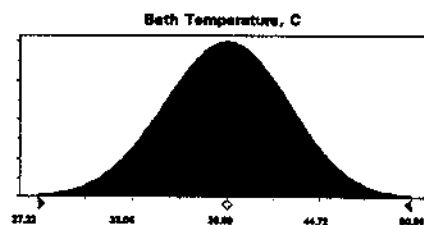
Parameter: Bath Surface Area, m^2
Lognormal distribution with parameters:

Log Mean	-0.11
Log Std. Dev.	0.33

Selected range is from 0.00 to 3.72
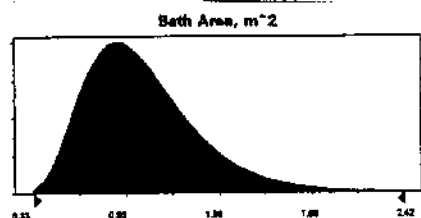Mean value in simulation was 0.94

Bath Area, m^2

Figure 6.
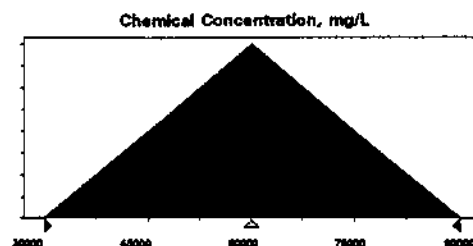# Parameter Assumptions for Unsparged Bath Monte Carlo Analysis - PDFs

Parameter: Chemical Concentration in Bath, mg/L
Triangular distribution with parameters:

Minimum	30000
Likeliest	60000
Maximum	90000

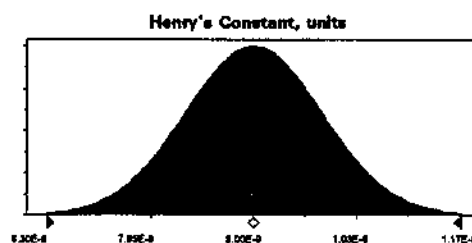Selected range is from 30000 to 90000
Mean value in simulation was 60000

Chemical Concentration, mg/L

Parameter: Henry's Constant, atm*m^3/mol
Normal distribution with parameters:

Mean	9.00E-09
Standard Dev.	9.00E-10

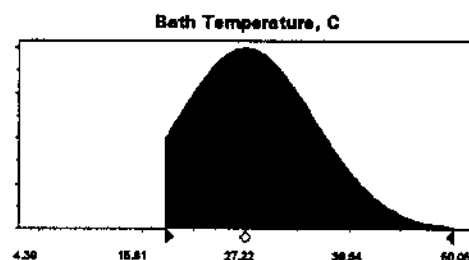Selected range is from 5.40E-9 to 1.26E-8
Mean value in simulation was 9.00E-9

Henry's Constant, units

Parameter: Bath Temperature, degrees C
Normal distribution with parameters:

Mean	27.22
Standard Dev.	7.61

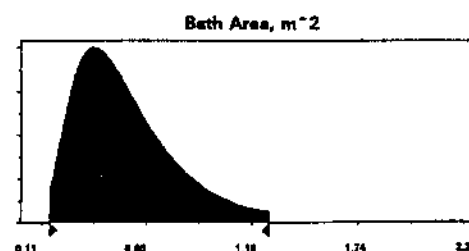Selected range is from 18.39 to 50.39
Mean value in simulation was 28.95

Bath Temperature, C

Parameter: Bath Surface Area, m^2
Lognormal distribution with parameters:

Geometric Mean	0.49
Geometric Std. Dev.	1.67

Selected range is from 0.15 to 1.28
Mean value in simulation was 0.53

Bath Area, m^2

Note: Process room volume and process room air turnover rate assumptions are the same as for formaldehyde (Figure 5).